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TOBACCO SMOKE FILTER

The present invention relates to tobacco smoke filters, especially for cigarettes.

The use of activated carbon to remove undesirable vapour phase (VP) components from tobacco smoke is well known.

There are over 400 compounds in the VP fraction of cigarette smoke (for example aldehydes, ketones and hydrocarbons). Activated carbon is a strong adsorbent; it is effective in removing a large number of these compounds from tobacco smoke. However, the compounds in the VP fraction all tend to be reduced by activated carbon to a similar extent; activated carbon may be described as an effective "blanket adsorbent".

In recent years, there has been a growing interest in selective filtration by cigarette filters, that is, the enhanced removal of specific compounds from tobacco smoke compared to removal of the other smoke components. One compound for which selective removal is particularly desirable is hydrogen cyanide (HCN), because HCN is generally recognised as being one of the most toxic compounds found in the VP fraction. HCN is removed by standard activated carbons when used in cigarette filters, but it is not selectively removed compared to other VP compounds. Indeed, its removal is usually lower than other VP compounds.

It is well known to add various chemicals to activated carbon to enhance the removal of particular compounds. These "impregnated carbons" are able to remove particular compounds through chemical reaction as well as by physical adsorption. Such carbons are used widely in, for example,

gas mask and respirator applications, where the activated carbon is generally impregnated with one or more of a number of chemical entities to target the removal of specific poisons. Our experiments have shown that such respirator-grade carbons are comparatively ineffective when used in cigarette filter applications because only low levels of overall removal are obtained. It is clear that respirator-grade carbons are not suited to a cigarette filter environment where contact times between the carbon and the gas are much less than those in gas mask/respirator applications. These respirator grade carbons also displayed little evidence of enhanced selectivity towards HCN. The above would lead one to expect that a high loading of impregnant would be required for effective removal of HCN in cigarette filter applications.

We have unexpectedly found that use of a relatively low level of impregnant, in combination with a base carbon having higher activity than that used in standard cigarette filters, is highly effective in removing HCN from cigarette smoke.

According to the present invention there is provided a tobacco smoke filter containing a high activity activated carbon impregnated with a metal impregnant.

Preferably the metal impregnant is present in an amount which is up to 10% of the dry weight of the high activity activated carbon. More preferably the impregnant is present in an amount which is from 1 to 5% of the high activity activated carbon. The metal impregnant may be, for example, one or more of copper, manganese, molybdenum, cobalt, iron, zinc. In one preferred embodiment, the impregnant is copper. In another preferred embodiment the

metal impregnant is a combination of copper and molybdenum.

In the present specification, by "metal impregnant", "copper" and "molybdenum" etc. it is meant the metals themselves and/or their ions, in any form (e.g. salts, complexes, chelates *etc.*).

The activated carbon of the invention may be derived from any raw material for which it is possible to prepare an activated carbon [these raw materials from which activated carbons may be prepared include, for example, wood, coal, nutshell such as coconut, peat, petroleum coke and bone; and synthetic sources such as poly(acrylonitrile) or phenol-formaldehyde].

The activated carbon is a "high activity" activated carbon. "Activity" in this context refers to percentage by weight of a particular vapour (e.g. carbon tetrachloride - CTC) adsorbed under equilibrium conditions by the base activated carbon (the base activated carbon refers to the activated carbon prior to impregnation by impregnant e.g. copper and/or molybdenum). Levels of activity herein are given as %CTC values. Thus, a value of carbon activity of 95%CTC refers to a level of adsorption of 95% by weight of CTC under equilibrium conditions. "High activity" refers to a base activated carbon (that is, an activated carbon prior to metal impregnation) which adsorbs more than about 90% CTC under equilibrium conditions. Preferably the activity is greater than 90% prior to impregnation. More preferably the activity of the activated carbon is greater than 100% prior to impregnation (that is, the base activated carbon adsorbs more than about 100% CTC under equilibrium conditions).

Preferably the activated carbon has an activity of greater than 80% CTC, more preferably greater than 90% CTC, after impregnation.

According to the present invention in a further aspect there is provided a tobacco smoke filter containing activated carbon which is impregnated with copper and molybdenum, wherein the ratio of copper to molybdenum is greater than 1.3 to 1.

A preferred ratio of copper to molybdenum (by weight) in the impregnated activated carbon is greater than 2:1. Particularly preferred are ratios of between 3.5:1 and 4.5: 1. A particularly preferred ratio of copper to molybdenum in the impregnated activated carbon is 4:1.

Preferably the activated carbon is a high activity activated carbon.

According to the present invention in a further aspect there is provided a tobacco smoke filter containing activated carbon which is impregnated with copper and molybdenum, wherein the activated carbon is a high activity activated carbon.

High activity activated carbons are discussed above. Preferably, the activity of the activated carbon is greater than 90% CTC, more preferably greater than 100% CTC.

Preferably the copper and molybdenum are present in a combined amount which is not more than 10% of the dry weight of the activated carbon. Preferably the copper and molybdenum are present in the activated carbon in an

amount which is from 1 to 5% of the dry weight of the activated carbon.

Preferably, the ratio of copper to molybdenum is greater than 1.3 to 1. More preferably, the ratio of copper to molybdenum is greater than 2 to 1, preferably between 3.5 to 1 and 4.5 to 1. A particular preferred ratio of copper to molybdenum is 4 to 1.

We have most unexpectedly found that a dramatic reduction of the metal impregnant concentration (e.g. the copper/molybdenum impregnant concentration), compared to the concentrations of impregnants commonly used in military or civilian respirators, does not lead to a discernable deterioration in the removal of HCN.

The particle size of the activated carbon of the invention depends on the performance required and the filter configuration. In the specification mesh sizes given are US Mesh. Suitable impregnated activated carbon is of particle size between 2mm (mesh size 10) and 0.15mm (100 mesh). Preferably, substantially all of the impregnated activated carbon is of particle size between 0.6mm (30 mesh)and 0.212mm (70 mesh). More preferably, substantially all of the impregnated activated carbon is of particle size between 0.425mm (40 mesh)and 0.212mm (70 mesh).

The impregnated activated carbon of tobacco smoke filters according to the invention may display surprising selective removal of HCN without detrimental effect on overall VP reduction. Impregnated carbons have not previously found favour in cigarette applications because chemical reactions between the impregnated component (e.g. metal ion) and components present in smoke (and/or the

products of these reactions) have a detrimental effect on the taste of the cigarette which reduces smoker satisfaction. The tobacco smoke filters of the invention may include a rather lower amount of *e.g.* impregnated copper, impregnated copper and molybdenum than previously thought necessary for acceptable removal of HCN; this is likely to reduce any adverse effects on taste.

The applicants have also shown that the benefits of the activated carbon of filters according to the invention are surprisingly effective at lower levels of activated carbon weight. This may reduce costs associated with filter manufacture. Preferred tobacco smoke filters contain less than 150mg activated carbon impregnated with metal impregnant (e.g. copper and molybdenum). Particularly preferred tobacco smoke filters contain from 10mg to 70mg impregnated activated carbon, more preferably 30mg to 60mg impregnated activated carbon.

The filter according to the invention may be of any design previously proposed for particulate adsorbent - containing tobacco smoke filters. For example the impregnated activated carbon according to the invention may be dispersed throughout the filter plug, carried on the tow or fibres or sheet material which is gathered to form the plug; it may instead adhere to one or more threads which extend through the matrix of the filter plug or be adhered to the inner face of a wrapper around the filter plug (as described for example in GB-A-9124535 and GB-A-9221545, to which attention is directed for more information); or it may form a bed sandwiched between a pair of plugs (e.g. of cellulose acetate tow) in a common wrapper.

Filters according to the invention may additionally include one or more particular adsorbents other than the

activated carbon required by the invention (e.g. silica gel, a different activated carbon or zeolite), which may or may not selectively remove other compounds present in the VP fraction of cigarette smoke (e.g. aldehydes). The additional adsorbent(s) may be mixed with the activated carbon required by the invention and/or separated from this.

Tobacco smoke filters according to the invention may also provide efficient removal of HCN even after prolonged periods (e.g. in storage) following filter or cigarette manufacture. The carbon used in known filters adsorbs volatile species present in the filter or tobacco during storage, thereby reducing the efficiency with which the filter carbon can remove VP compounds when the cigarette is smoked. This has the result that the efficiency with which the known filters remove HCN also decreases on ageing. Surprisingly, the ability of filters according to the invention to remove HCN does not deteriorate significantly even after storage for prolonged periods (e.g. six months).

The present invention also provides a filter cigarette comprising a filter according to any preceding claim joined at its upstream end to a wrapped tobacco rod. The cigarette filter according to the invention will usually be attached to a wrapped tobacco rod with conventional tipping overwrap, which may be a ventilated or non-ventilated overlap.

The invention is illustrated by the following examples and with reference to the attached drawings, in which Figs. 1 and 2 respectively are schematic sectional side elevation views, not to scale, of an individual filter and filter cigarette according to one embodiment of the

invention; and Fig. 3 is a schematic sectional side elevation view, not to scale, of an individual filter according to a different embodiment of the invention.

Comparative examples - respirator carbons

Numerous impregnated commercial carbons recommended for the removal of HCN in respirator applications were obtained from a number of suppliers and compared to a standard (unimpregnated) carbon used routinely in cigarette filter applications. These tests involved assembling cigarettes with "triple granular" filters, each containing 100mg of activated carbon in a packed bed between two cellulose acetate filter segments. The filter cigarettes were smoked under ISO conditions ($35cm^3$ puffs, each of two-second duration, taken once per minute) and the Hydrogen Cyanide HCN and mean VP yields were measured. The percentage reductions in mean VP and HCN for cigarettes A to F (each of which includes one of six typical respirator grade activated carbons) as compared to an equivalent cigarette containing no carbon in the filter are given in Table 1. The Table also includes the VP and HCN values for a "Standard" cigarette containing a filter which includes an unimpregnated activated carbon derived from coconut shells (as typically used in cigarette filters).

Table 1

Sample reference (Sample ref.)	Mean VP reduction (%)	HCN Reduction (%)
Standard	55	44
A	22	23
B	27	31
C	25	41
D	29	47
E	23	46
F	39	36

It is clear that the respirator samples A to F are not suitable for a cigarette filter environment. It is also clear that the Standard filter is not selective for HCN.

Preparation of Impregnated samples

Samples of impregnated activated carbon were prepared typically by dissolving basic copper(II) carbonate, ammonium carbonate and ammonium dimolybdate(VI) into an aqueous, ammoniacal solution and mixing with the activated carbon according to the ratios detailed in Table 2 (given for 2% copper; 0.5% molybdenum). Quantities for other metal concentrations (and ratios) were adjusted accordingly. The resulting slurry was heat treated to 175°C to give a dry, free flowing product, which was then screened to the required mesh size.

Table 2

Components	**Weight (g)**
activated carbon	1000
basic copper(II) carbonate	44
ammonium dimolybdate(VI)	12
ammonium carbonate	20
water	460
ammonia solution (0.88)	158

Testing of Impregnated Samples

Fourteen impregnated activated carbon samples were prepared by the method above. Filter cigarettes were assembled, each containing 100mg of one of the samples, and tested using the procedures described for the comparative samples above. The results for the fourteen impregnated samples, and for two unimpregnated controls (Sample Refs. 3 and 4), are given in Table 3.

A further sample of impregnated carbon containing 2% copper only was prepared using the procedure described above, with the exception that ammonium dimolybdate was omitted from the mix. The sample(Sample Ref 27) was tested using the same procedure as that used for the samples included in Table 3, and the results are given in Table 3a.

Table 3

Sample Ref.	Carbon activity (% CTC) Base	Carbon activity (% CTC) Impregnated	Metal Content (%)*	Mesh size (US Mesh)	Mean VP Reduction (%)	HCN Reduct -ion (%)
1	80	46	>10	20/40	29	46
2	80	47	>10	12/20	15	25
3	95	n/a	nil	30/70	77	75
4	60	n/a	nil	30/70	51	53
5	101	75	10	30/70	42	92
6	122	82	10	30/70	66	93
7	101	84	5	30/70	56	92
8	103	91	5	30/70	64	83
9	80	73	5	30/70	69	93
10	83	75	5	30/70	46	58
11	101	91	2.5	30/70	81	88
12	101	95	1.25	30/70	83	88
13	101	91	2.5	30/70	77	82
14	108	99	2.5	12/20	57	70
15	125	111	2.5	30/70	90	91
16	125	111	2.5	12/20	65	74

* Expressed as (Copper + molybdenum) in the ratio 4:1.

Table 3a

Sample Ref.	Carbon activity (% CTC) Base	Carbon activity (% CTC) Impregnated	Metal Content (%) (Copper)	Mesh size (US Mesh)	Mean VP Reduction (%)	HCN Reduct-ion (%)
27	100	95	2.0	20/40	80	82

The results show that in order to achieve a high reduction of VP material (that is reduction of components in the VP fraction of cigarette smoke) in combination with a high reduction of HCN (reduction of HCN in the VP fraction of cigarette smoke), in cigarette filters which are embodiments of the present invention such as Sample Refs 11, 15 and 27, it is desirable to use a base carbon with a high activity (greater than around 90% CTC) in combination with a comparatively low level of metal impregnation (less than 10%, preferably 1 to 5%).

The higher CTC activities tend to have both a higher HCN retention and VP retention. VP retention increases with decreasing impregnant concentration. HCN retention remains fairly constant when measured as a function of copper and molybdenum concentration (Table 3). It is therefore surprising that a dramatic reduction of the copper/molybdenum impregnant concentrations, relative to those used in civilian or military respirators, has resulted in no discernible deterioration of the removal of HCN by filters containing these carbons.

Activated carbons derived from different base materials (e.g. coconut shell and coal) have been prepared; these show there is little difference in terms of HCN retention

between, for example, coal and coconut for the same mesh size, level of impregnation and activity.

The results also clearly show that smaller mesh sizes (e.g. mesh size 30/70 US mesh) give superior performance in terms of HCN than the larger mesh sizes (compare, for example, Samples 15 and 16). This is contrary to customarily observed behaviour in cigarette filters, where variations in mesh size have been found to have only a relatively minor effect on VP removal.

Our experiments have also shown that the comparative benefits of the activated carbon in embodiments of the invention are even more pronounced at lower levels of carbon weight in the filter. Sample Refs 8 and 11 were used in the manufacture of cigarette filters having two different carbon weights (i.e. 5% and 2.5% metal levels respectively) and tested as described above. The results are given in Tables 4a and 4b.

Table 4a - Cigarette filter including Sample Ref 8.

Carbon weight (mg/cig)	Mean VP reduction (%)	Mean HCN reduction (%)
95	76	87
50	40	80

Table 4b- Cigarette filter including Sample Ref 11.

Carbon weight (mg/cig)	Mean VP reduction (%)	Mean HCN reduction (%)
95	72	90
50	56	80

Retention of performance over time

A disadvantage of known carbon containing filters is that the carbon in the filter adsorbs volatile species present in the filter or tobacco during storage, thereby reducing the efficiency with which the carbon can remove VP compounds on smoking. This has the effect that the overall efficiency with which known carbons remove HCN reduces on aging. The applicants tested the change in performance of filter cigarettes which included filters which embody the invention. The filters included approximately 95mg of carbon per filter.

The filters embodying the invention where stored as assembled cigarettes and the change in performance was measured at 0, 3 and 6 months. The results are shown in Table 5.

Table 5

Age	Standard carbon* Mean redn.		Sample Ref. 8 Mean redn.		Sample Ref. 11 Mean redn.	
months	VP (%)	HCN(%)	VP (%)	HCN(%)	VP (%)	HCN(%)
0	64	53	76	87	72	90
3	55	41	62	86	63	88
6	45	29	48	85	50	85

* carbon tested in table 1

It is clear that the HCN reduction (redn.) performance of filters which embody the invention, those made with Sample Refs. 8 and 11, is not significantly reduced over six months (especially compared to the sample containing standard carbon).

Figs. 1 and 2 respectively are schematic sectional side elevation views, not to scale, of an individual filter and filter cigarette according to one embodiment of the invention.

The Fig.1 filter has a cylindrical buccal end filtering plug 2 of cellulose acetate tow, a cylindrical upstream filtering plug 3 of cellulose acetate tow, and a filter wrapper 4 engaged around the plugs to form a cavity 6 therebetween. The cavity 6 is filled with granules 17 of activated carbon impregnated with copper and molybdenum prepared according to the methods above and of identical composition to sample ref 11 described above.

Fig.2 shows a filter of the Fig.1 type joined at its upstream end 7 to a tobacco rod 10 in its own wrap 11 by means of a full tipping overwrap 12 which surrounds and engages the full length of the filter and the adjacent end only of the wrapped tobacco rod 10, 11.

Example 17

In a specific example of a filter and filter cigarette according to the invention as described with reference to Figs.1 and 2, the filter is 27 mm long and about 25 mm in circumference. The buccal end plug 2 is a 10 mm long non-wrapped acetate (NWA) plug - i.e. a preformed non-wrapped plug of plasticised cellulose acetate filaments gathered and bonded together such as is well known in the art.

The upstream end plug 3 is a 10 mm long wrapped acetate (WA) plug - i.e. a preformed wrapped plug of plasticised cellulose acetate filaments. The filter wrapper is 27 mm long to give a cavity 6, which is 7 mm long,

extending between plugs 2 and 3. The cavity 6 is filled with 100mg of granules 17 of activated carbon impregnated with copper and molybdenum prepared according to the methods above and of identical composition to sample ref 11 described above. The filter rod is attached by a ventilating tipping overwrap 12 to a commercial wrapped tobacco rod 10, 11.

In a further specific Example (Example 17a), the cavity is filled with 100 mg of granules 17 of activated carbon impregnated with copper prepared according to the methods above and of identical composition to Sample Ref. 27 described above.

It will be appreciated that Example 17 and Example 17a are similar in construction to a known triple granular filter but include activated carbon according to the invention.

Fig. 3 is a schematic sectional side elevation view, not to scale, of an individual filter according to a different embodiment of the invention.

The Fig 3 filter has a cylindrical buccal end filtering plug 52 of cellulose acetate tow and a cylindrical upstream filtering plug 53, also of cellulose acetate tow. Particles 67 of activated carbon impregnated with copper and molybdenum prepared according to the methods above and of identical composition to sample ref 11 described above are dispersed throughout the upstream filtering plug 53, carried on the tow or fibres or sheet material which is gathered to form the plug. A filter wrapper 54 is engaged around the plugs. It will be appreciated that a filter of the Fig.3 type may be

joined at its upstream end 57 to a tobacco rod in the manner shown with reference to Example 17 in Fig 2, for example (e.g. joined to the tobacco rod in its own wrap by means of a full tipping overwrap which surrounds and engages the full length of the filter and the adjacent end only of the wrapped tobacco rod).

Example 18

In a specific example of a filter according to the invention as described with reference to Fig 3, the filter is 27 mm long and about 25 mm in circumference. The buccal end plug 52 is a 14 mm long non-wrapped acetate (NWA) plug - i.e. a preformed non-wrapped plug of plasticised cellulose acetate filaments gathered and bonded together such as is well known in the art.

The upstream end plug 53 is also a 13 mm long preformed plug of plasticised cellulose acetate filaments gathered and bonded together such as is well known in the art. 50mg of particles 67 of activated carbon impregnated with copper and molybdenum prepared according to the methods above and of identical composition to sample ref 11 described above are dispersed throughout filtering plug 53, carried on the tow material (filaments) that was gathered to form the plug. The methods by which the particles may be introduced to the tow material during the gathering process are well known in the art. A filter wrapper 54 is engaged around the plugs and is 27 mm long.

The filter rod may be attached by a ventilating tipping overwrap to a commercial wrapped tobacco rod in the manner shown in Fig 2 and described with reference thereto.

In a further specific Example (Example 18a), the cavity is filled with 50 mg of particles 67 of activated carbon impregnated with copper prepared according to the methods above, and of identical composition to Sample Ref.27 described above, dispersed throughout filter plug 53, carried on the tow material.

It will be appreciated that Examples 18 and 18a are similar in construction to a known active acetate filter but include activated carbon according to the invention.

It will be appreciated that the filter according to the invention may be of any design previously proposed for particulate adsorbent - containing tobacco smoke filters with the substitution of the known particulate adsorbent with the impregnated activated carbon of the invention.